THE CONDUCTIVITY AND VISCOSITY OF SOLUTIONS OF LITHIUM NITRATE IN CERTAIN MIXED SOLVENTS

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SAMUEL RILEY SPENCER

A.B., Baylor University, 1911

DISSERTATION

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Submitted in Partial Fulfillment of the Requirements for the

DEGREE OF

DOCTOR OF PHILOSOPHY

IN

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The author wishes to express to Dr. James Lawrence Whitman, under whose direction this work was carried out, appreciation for his manifest interest in the work and for the valuable help which he has so graciously rendered; without which the labor would have been greatly increased.

THE CONDUCTIVITY AND VISCOSITY OF SOLUTIONS OF LITHIUM NITRATE IN CERTAIN MIXED SOLVENTS

As part of some investigations being carried on in this Laboratory, it was found desirable to make a series of measurements of the conductivity and viscosity of solutions of lithium nitrate in mixtures of methyl alcohol and ethyl alcohol, and of methyl alcohol and water. Such measurements have previously been made by Jones and Lindsay[1] and by Jones and Carroll,[2] but it seems desirable to report the more extended series of measurements which we have made.[3]

Materials

Lithium Nitrate.—This was prepared from pure lithium carbonate and C. P. nitric acid, was recrystallized five times from conductivity water and was then shown to be free from impurities by a spectroscopic test. The drying of the salt was found to be more difficult than would be indicated from the literature. Anhydrous material could only be obtained by prolonged heating at 150° in a vacuum. This probably accounts for the fact that the values here recorded are uniformly higher than the values previously reported.

Water.—Laboratory distilled water was electrically redistilled from alkaline permanganate and had a conductivity of 1 to 1.2 $\times 10^{-6}$.

Alcohol.—A good grade of ethyl alcohol was successively treated with lime, metallic calcium, silver nitrate and finally again with lime prepared according to Danner and Hildebrand.[4] Thus prepared it had a conductivity of about 3 $\times 10^{-7}$, while methyl alcohol prepared in a similar manner had a conductivity of 2 $\times 10^{-6}$.

Solutions.—Dry lithium nitrate was weighed into a quartz flask, solvent of the required composition then being added to give a solution of the greatest desired concentration. More dilute solutions were made by adding solvent in the required amount to this stock solution.

Apparatus and Measurements

A Leeds and Northrup Kohlrausch slide wire bridge with extension coils, a microphone hummer, tunable head phones, Curtis coil resistance boxes, adjustable air con-

[1] Jones and Lindsay, *Am. Chem. J.*, **28**, 329 (1902).

[2] Jones and Carroll, *ibid.*, **32**, 521 (1904).

[3] For a summary and review of the work of Jones in the field of conductivity in mixed solvents see Jones and Kreider, *ibid.*, **45**, 282 (1911).

[4] Danner and Hildebrand, *J. Am. Chem. Soc.*, **44**, 2824 (1922).

densers and the usual sheathings and shieldings were used. The grounded water-bath consisted of a heavy Pyrex vessel of about 12 liters' capacity, the temperature being regulated to 25 ± 0.01°. Washburn pipet cells were calibrated by the method of Kraus and Parker.[5] All other apparatus was carefully calibrated and from 8 to 15 resistance measurements were made on each solution used. All values were corrected for the conductivity of the pure solvent.

Viscosity measurements were made in an Ostwald type quartz viscosimeter.

Experimental

Methyl Alcohol–Ethyl Alcohol Mixtures.—The equivalent conductivities of solutions of lithium nitrate of various concentrations and in solvents ranging in composition from pure methyl alcohol to pure ethyl alcohol are recorded in Table I. In every solvent used the equivalent conductivity increases with dilution as is normally the case with water solution, but in no case does the Mass Law hold. For the more dilute solutions the conductivity is almost exactly a linear function of the composition of the solvent, and even for the 0.1 molar solution the deviation is small. The viscosities of a series of mixtures of the two alcohols are given in Table II, referred to water at 25° as unity.

TABLE I

THE EQUIVALENT CONDUCTIVITY OF LITHIUM NITRATE IN METHYL ALCOHOL, ETHYL ALCOHOL AND IN MIXTURES OF THESE SOLVENTS AT 25°

Concn., molar	100% CH_3OH	90%	80%	70%	60%	50%	40%	30%	20%	10%	100% C_2H_5OH
0.1	54.27	50.56	45.71	41.83	37.05	33.84	30.16	26.88	23.62	21.01	17.47
.05	63.07	58.10	53.17	49.19	43.87	40.12	35.82	32.04	28.36	24.69	20.74
.025	71.27	65.49	59.30	55.73	49.77	45.95	41.05	36.96	32.75	29.07	24.07
.0125	78.88	72.21	66.30	61.92	56.33	51.49	46.11	41.57	37.05	32.09	27.36
.00625	84.70	78.51	72.36	67.16	61.85	56.35	50.82	45.81	41.17	36.10	30.40
.003125	89.30	83.87	77.91	71.21	64.41	61.03	54.82	49.92	45.06	39.22	33.25
.001562	93.10	87.85	81.84	75.21	69.87	65.09	59.50	53.34	47.40	41.12	35.10
.000781	95.63	91.40	85.16	79.11	73.15	67.52	62.10	56.05	50.05	44.08	38.13
.000391	99.59	94.02	88.10	82.24	76.05	70.51	64.85	59.24	53.19	47.31	41.10
.000195	104.17	98.12	92.18	86.15	80.21	74.31	67.81	62.14	55.91	50.08	44.16

TABLE II

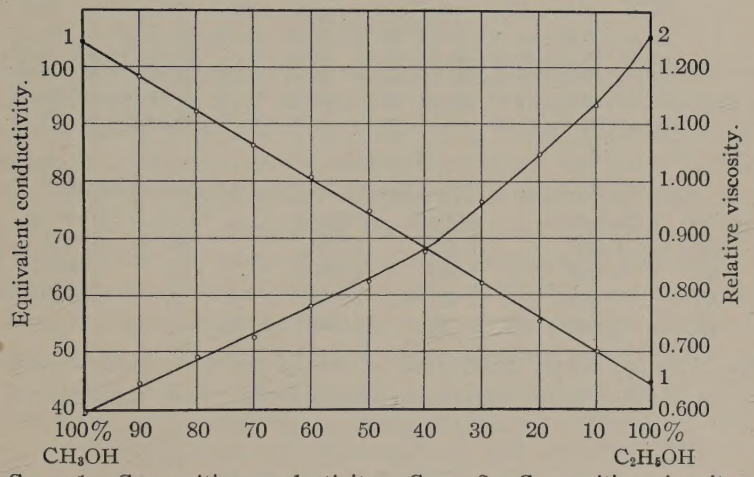
THE VISCOSITY OF METHYL ALCOHOL–ETHYL ALCOHOL MIXTURES AT 25°

CH_3OH, %	Viscosity	CH_3OH, %	Viscosity	CH_3OH, %	Viscosity
100	0.5968	60	0.7800	20	1.0477
90	.6400	50	.8262	10	1.1310
80	.6826	40	.8785	0	1.2530
70	.7249	30	.9618	..	....

In Fig. 1, Curve 1, composition of solvent is plotted against equivalent conductivity for the most dilute solution; in Curve 2 composition is plotted against viscosity for the pure solvent. Viscosity determinations were made for a number of the more dilute solutions but the values obtained differed so little from those for the pure solvents of the same composition that the latter values have been used in all cases.

[5] Kraus and Parker, *J. Am. Chem. Soc.*, **44**, 2422 (1922).

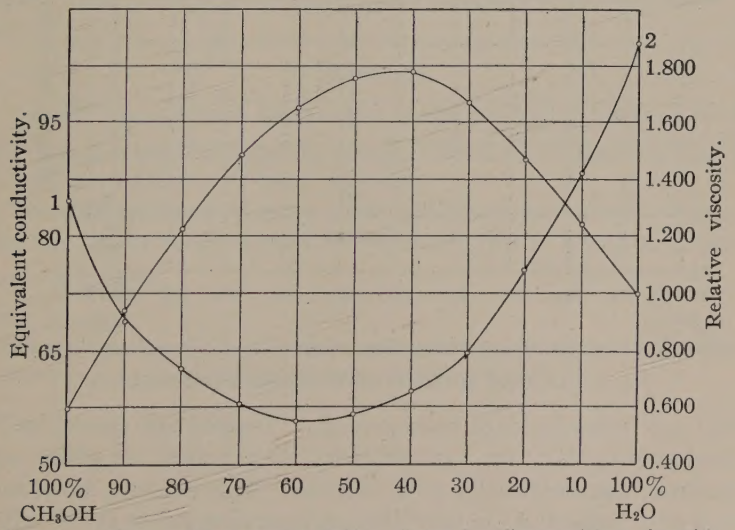
Methyl Alcohol–Water Mixtures.—Table III gives the equivalent conductivities for a series of solutions of lithium nitrate in various mixtures of methyl alcohol and water. Viscosities of the same mixtures are given



Curve 1.—Composition–conductivity. Curve 2.—Composition–viscosity.

Fig. 1.—Lithium nitrate in methyl alcohol–ethyl alcohol mixtures.

in Table IV. Dilution was not carried as far as with the methyl alcohol–ethyl alcohol mixtures, since it was found that at a concentration of 0.00625



Curve 1.—Composition–conductivity. Curve 2.—Composition–viscosity.

Fig. 2.—Lithium nitrate in methyl alcohol–water mixtures.

molar the viscosity of the solution did not differ appreciably from that of the pure solvent. The corresponding curves are shown in Fig. 2.

TABLE III

THE EQUIVALENT CONDUCTIVITY OF LITHIUM NITRATE IN WATER, METHYL ALCOHOL AND IN MIXTURES OF THESE SOLVENTS AT 25°

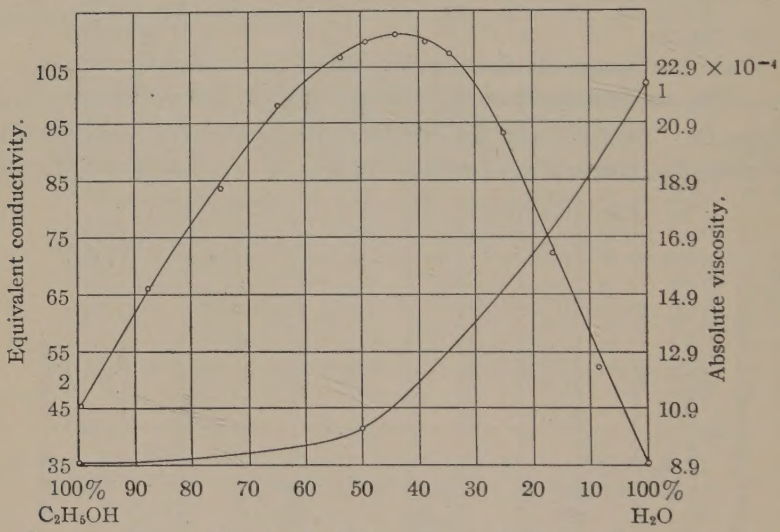
Concn. molar	100% H_2O	90%	80%	70%	60%	50%	40%	30%	20%	10%	100% CH_3OH
0.1	90.56	75.09	64.01	54.95	50.25	47.14	45.50	49.91	47.15	49.82	54.27
.05	94.84	79.31	66.85	57.71	53 07	50.01	48.37	49.21	51.40	54.96	63.07
.025	98.87	83.05	70.04	60.23	55.54	52.40	51.05	52.24	55.20	59.81	71.27
.0125	102.14	85.85	72.77	62.57	57.97	54.70	53.47	55.17	58.99	64.68	78.88
.00625	105.45	88.43	75.91	64.75	60.04	56.60	55.56	58.00	62.95	68.87	84.70

TABLE IV

THE VISCOSITY OF WATER–METHYL ALCOHOL MIXTURES AT 25°

H_2O, %	Viscosity	H_2O, %	Viscosity	H_2O, %	Viscosity
100	1.000	60	1.781	20	1.229
90	1.240	50	1.760	10	0.9473
80	1.466	40	1.656	0	.5969
70	1.667	30	1.483	..	....

Ethyl Alcohol–Water Mixtures.—Data of previous authors are used for ethyl alcohol–water mixtures, conductivity data from Jones and



Curve 1.—Composition–conductivity. Curve 2.—Composition–viscosity.

Fig. 3.—Lithium nitrate in ethyl alcohol–water mixtures.

Lindsay[1] and viscosity data from Noack.[6] Graphs are shown in Fig. 3. The conductivity data are unsatisfactory since values are given only for one mixture, that containing 50% alcohol. It is evident, however, and is so stated by Jones and Lindsay[7] that no minimum exists at 25°, although a slight minimum is found for certain concentrations at 0°. An examina-

[6] John C. Evans, "Physico-Chemical Tables," Griffin and Co., Ltd., London, 1911, p. 651.

[7] Ref. 2, p. 362.

tion of Fig. 3 shows that a decided maximum occurs in the composition–viscosity curve, in this respect being similar to the methyl alcohol–water mixtures.

Discussion

Jones and Lindsay[1] and Jones and Carroll[2] studied solutions of several salts in mixtures of methyl alcohol and water. Measurements were made at various concentrations and at 0 and 25°. They concluded that "the minimum of conductivity is caused primarily by the great decrease of fluidity resulting when the two components of the mixture are brought together."[8] Without considering the many dilutions used, 23 distinct cases were studied, of which 9 show a very pronounced minimum in the conductivity curve, 3 show a slight minimum, while 11 show no minimum.[9] The very marked minimum occurs only in the methyl alcohol–water mixtures, while in the ethyl alcohol–water mixtures the minimum occurs only at 0°, and then only occasionally. For calcium nitrate no minimum appears under any conditions. These results are difficult to interpret in terms of viscosity, especially in view of the fact that one of the common arguments in favor of the relationship between viscosity and conductivity is that the temperature coefficients of the two are nearly the same.

We have verified and extended Jones' results for the methyl alcohol–water mixtures and have obtained data for methyl alcohol–ethyl alcohol mixtures. The work is being continued to include a number of the higher alcohols.

Summary

1. Measurements have been made of the conductivities and viscosities of solutions of lithium nitrate in water, methyl alcohol and ethyl alcohol, and in various mixtures of these solvents.

2. The difficulties involved in drying lithium nitrate have been pointed out and are shown to be a possible source of error in previous work.

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[8] Ref. 2, p. 553.

[9] Three of this group show a very slight minimum at one concentration. The reader is referred to the original article for a complete comparison.

BIOGRAPHY

Samuel Riley Spencer was born near Sanger, Texas, July 11, 1874. He grew to manhood on a farm near Decatur, Texas. His grade school education was received in the rural schools. Owing to circumstances over which he had no control, he was deprived of high school education until 1898, at which time he entered the academy of Decatur College, a Junior College located at Decatur, Texas. He graduated from Decatur College in 1905, and taught in that institution until 1909. In the fall of 1909 he entered Baylor University, where he received the Bachelor of Science degree of 1911. From 1911 to 1915 he was instructor in chemistry in Baylor University. During the scholastic year 1915–16, he was a graduate student in Yale University. He was also a graduate student in Chicago University during the summers 1913, 1916, 1917 and 1921. From 1917 to 1924 he was Professor of Physics and Dean of the College of Liberal Arts in Baylor University. Since that time he has been engaged in graduate work at the University of Iowa. He is a member of the American Physical Society.